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SOME COMPONENTS OF SEDIMENT OXYGEN DEMAND IN LAKE ERIE SEDIMENTS

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ABSTRACT

We have examined SOD of Lake Erie sediments with and without macrobenthic infauna, and with high and low macrobial activity, and have modeled the penetration of oxygen into sediments, since the depth of oxygen penetration is not easily measured. SOD of western and central basin sediments (95% silt clay, 3% organic carbon, 70-80% water content) ranges from 1.25-2.5 μm O_2/hr in laboratory microcosms. When tubificid oligochaetes are added to laboratory microcosms (30,000 m^{-2}), SOD rises to 1.5-3.5 μm O_2/hr. SOD is greater than the simple sum of organism respiration plus sediment SOD. The extra enhanced demand is due to enhanced microbial activity, the transport of O_2 to greater depths in the sediment, and to the transport by feeding of FeS to the sediment-water interface. Enhanced demand over sediment plus respiration values appear to be proportional to the number of oligochaetes present, which would implicate FeS transport as a major factor in enhanced demand. Thus, tubificids enhance the rate of organic decay not only through aiding the transport of dissolved oxygen, but also by transporting reduced sulphur to be oxidized to SO_4^{2-} at the sediment-water interface. Sediment sterilization techniques were not successful; these techniques probably result in the release of additional oxygen demanding substances as a result of sterilization. There is a pattern of decreasing SOD for a period of about 10-14 days after the start of an experiment until an equilibrium SOD is reached. This is due to the liberation of bacterial nutrients when sediments are added to microcosms and mixed. Thus experiments done soon after introduction of sediments into an SOD apparatus are likely to be in error by as much as a factor of two.

FIGURES

TABLES

BACKGROUND

The research covered by this report is an outgrowth of the work of McCall and Fisher (1980) in which the oxygen consumption of Lake Erie sediment and tubificid oligochaetes was measured in the laboratory. The oxygen consumption of Lake Erie sediment inhabited by tubificid oligochaetes was found to be approximately twice as great as the sum of tubificid respiration and SOD of lake sediment without tubificids. McCall and Fisher (1980) attributed this increase in SOD to a combination of the flux of reduced FeS to the sediment surface due to tubificid feeding and increased microfial respiration due to tubificid burrowing and excretion. The additional research described herein was conceived to test the theory about the transport of FeS to the surface by oligochaetes and to estimate the major components of SOD.

CONCLUSIONS AND RECOMMENDATIONS

Tests were performed to measure oligochaete respiration as well as chemical and microbial oxygen demand or consumption. Oligochaete respiration reported here (0.061 - 0.079 $\frac{\mu \text{ Mol } O_2}{\text{Mg wet mass/day}}$) is larger than the value reported by McCall and Fisher (1980). Some evidence was also found that suggests oligochaetes secrete ammonia directly. Chemical and microbial oxygen consumption at steady-state was found to have a range of about 1.25-2.50 $\frac{\mu \text{ Mol } O_2}{\text{Hr}}$. The upper value of the range agrees quite well with the value reported by McCall and Fisher (1980).

Other tests were performed to measure the oxygen consumption of sediment with 130 oligochaetes present. The values of oxygen consumption reported here for this case are 1.53 and 3.47 $\frac{\mu \text{ Mol } O_2}{\text{Hr.}}$. The lower value looks quite low when compared to the steady-state curve reported here. Even the larger value of 3.47 cannot be compared directly to McCall and Fisher (1980), because a smaller number of oligochaetes were used in the work reported here. However, the 3.47 can be scaled-up to the number of oligochaetes (456) used by McCall and Fisher (1980), and the resulting calculated value is 5.90 $\frac{\mu \text{ Mol } O_2}{\text{Hr.}}$ which compares quite well with the value of 6.72 ± 0.03 $\frac{\mu \text{ Mol } O_2}{\text{Hr.}}$ reported by McCall and Fisher (1980).

Sediment samples were irradiated to destroy both macro and micro organisms to measure chemical oxygen demand or consumption directly. Unfortunately the attempt was not successful, and there is no obvous explanation. The method was different than the one used by McCall and Fisher (1980), but the results are similar.

Oxygen consumption models were constructed and tested using oxygen profile data reported by Revsbech et al., (1980). Several assumptions were made regarding the kinetics of oxygen consumption. In general the models reproduced the data reasonably well but not exactly.

It is recommended that testing be continued to measure pore water concentrations of FeS so that the flux of FeS from the sediment can be calculated. The oxygen consumed in oxidizing FeS could then be calculated. A test to measure the oxygen consumption of oligochaete fecal pellets, which contain FeS should also be performed. Work should also continue on separation of chemical and microbial consumption. This will help form a clearer picture of Lake Erie sediment oxygen demand.

A better electrode could be found for continuous monitoring of oxygen consumption than the one used here.

Finally, as one of the purposes of this study is to provide data to facilitate the construction of models to predict sediment oxygen demand, research directed toward constructing such models should continue.

INTRODUCTION

The Laurentian Great Lakes make up the largest continuous freshwater body in the world; the lakes contain about 20% of the world's fresh water supply. Nearly 20% of the U.S. population lives in the Great Lakes drainage basin that is the industrial heartland of North America. The major portion of the gross national products of the U.S. and Canada is generated here. The lakes are used as a drinking water supply, a source for industrial process water, commercial shipping, a food supply, and recreation. These uses are often conflicting. For instance, the dredging of harbors and disposal of dredged materials that is necessary for continued commercial shipping may affect lake water quality. Envirnonmental managers need some rational criteria for resolving conflicting demands on this ecosystem.

Eutrophication is a persistent feature of many lakes like Lake Erie that have large ratios of basin surface to water volume that are located in large drainage basins. The input of nutrients to such lakes results in very high algal productivity. When algae die they settle to the bottom of the lake and are decomposed by bacteria. The water in temperate lakes is commonly thermally stratified in the summer and exchange of bottom water with the atmosphere is limited. The decomposition of algae and other organic matter at the lake bottom consumes oxygen, and the bottom waters of the lake may become completely anoxic. This has many important effects. Toxic materials sequestered in reduced sediments may be freed to flux into the overlying water. Commercially desirable fish are not able to inhabit large parts of the lake. The growth of algal species that have undesirable effects on water quality (taste and odor) is encouraged.

The oxygen demand of bottom sediments varies from time to time and place to place in one lake and from one lake to another. Lake sediments constitute a complex biogeochemical system and causes for variations in sediment oxygen

demand are not well known. The sources of sediment oxygen demand may be divided into at least three categories: 1) microbial oxygen demand (bacteria, protozoa); 2) macrofaunal oxygen demand (primarily tubificid oligochaetes and insect larvae); and 3) chemical oxygen demand of inorganic oxidation of reduced chemical compounds. However, another major component of SOD in Lake Erie sediments has been suggested (McCall and Fisher, 1980). Tubificid oligochaetes feed at depth in the reduced zone of the sediment and deposit fecal material at the sediment-water interface. This reduced material, such as FeS, increases the consumption of oxygen.

The relative contribution of all of these sediment components to total sediment oxygen demand has never been measured in a single lacustrine environment. Knowing the major components of sediment oxygen demand in Lake Erie should lead to better explanations of temporal and spatial variations of sediment oxygen demand, enable environmental managers to construct more realistic models of oxygen depletion in lakes, and provide insight into the post-depositional degradation of organic matter in freshwater sediments. In the research covered by this report, we attempt to estimate values for the major components of sediment oxygen demand in Lake Erie.

REVIEW OF RELATED RESEARCH

In shallow lakes, sediments are an important site of detrital decomposition, and, consequently, oxygen consumption. In highly productive lakes, the sediment oxygen demand engendered by the decay of sedimenting organic matter may be sufficient to cause hypolimnetic anoxia. In the central basin of Lake Erie, SOD accounts for 81% of the oxygen consumed (Burns and Ross, 1972). As a result of this demand, the hypolimnion of Lake Erie's central basin is subject to complete oxygen depletion during late summer (Dobson and Gilbertson, 1972). Of all the profound changes produced by hypolimnetic anoxia, the one of singular interest is the release of algal nutrients from their sediment store (Mortimer, 1941; 1942; 1971). Such release of nutrient materials during anoxia raises the possibility of cyclic self-fertilization in the lake. Since the consumption of oxygen by sediments is of such great importance to the "health" and utility of an ecosystem such as Lake Erie, it is critical to understand the process of sediment oxygen demand.

Sediment oxygen demand is a combination of the oxygen demands for respiration by the resident benthic community (macrobenthos, meiobenthos, and microbenthos), and for the oxidation of reduced chemical species reaching the sediment-water interface.

Total SOD and some components of SOD have been measured in a number of environments (Teal and Kanwisher, 1961; Carey, 1967; Mconnell and Hall, 1969; Pamatmat, 1971a,b; Smith, 1973; Hale, 1975), but none of these studies examine the effects of macrofaunal organisms on sediment physical properties and chemistry. Through feeding, burrow construction, and other life activities, macrobenthos alter the physical and chemical nature of surficial sediments. As a consequence, in the presence of certain macrobenthos, more oxygen is consumed by a sedimentary deposit than can be accounted for by organismal respiration and molecular diffusion alone

(Edwards, 1958; Neame, 1975). Working with sediments inhabited by benthic insect larvae, both Edwards (1958) and Neame (1975) concluded that the sediment stirring and water pumping activities of these organisms could account for this discrepancy, and that molecular diffusion of oxygen supply was increased when macrobenthic insect larvae are reasonably abundant.

Tubificid oligochaetes are the most abundant macrobenthos in Lake Erie, but unlike many benthic insect larvae, they do not pump significant volumes of water across the sediment-water interface (McCall and Fisher, 1980). However, these organisms feed on material within the anaerobic zone of the sediment column, and egest fecal pellets which contain oxygen demanding materials such as FeS, at the sediment-water interface. Concomitantly, oxidized material at the sediment-water interface is subducted to depth in the sediment where it is reduced (Robbins et al., 1979; McCall, 1979).

McCall and Fisher (1980) measured oxygen consumption of Lake Erie sediment and oligochaetes in laboratory respirometers under various environmental conditions (Table 1), and found that the oxygen consumption of tubificid inhabited lake sediment was twice the simple sum of tubificid respiration and SOD of lake sediment without tubificids (Table 1). They attributed this increase in SOD to a combination of increaed SOD due to flux of reduced FeS by tubificid feeding and enhanced microbial respiration due to tubificid burrowing and excretion.

In addition to research to measure SOD, other research has been performed in an attempt to determine oxygen profiles as a function of time. Recent technological advancements in the measurement of dissolved oxygen have enabled the determination of detailed oxygen profiles in recent sediments (Revsbech et al., 1980) have been used to calculate the flux of oxygen across the sediment-water interface.

Table 1. Oxygen consumption results.

CASE	CONDITION	OXYGEN CONSUMPTION COMPONENTS	BLANK ADJUSTED O_2 CONSUMPTION $\mu M\ O_2$/hr.
a	kaolin sediment	S	
b	kaolin sediment + *T. tubifex*	S + T	.90 ± .02
c	lake sediment	S + M + C	2.26 ± .03
d	lake sediment + *T. tubifex*	S + M + C + T	6.72 ± .03

S = measurement system oxygen demand
T = *T. tubifex* oxygen demand
M = microbial oxygen demand
C = chemical oxygen demand

GEOCHEMICAL CONSIDERATIONS

As one of the components of SOD is chemical oxygen demand, a number of possible chemical reactions were considered to ascertain potential impact on oxygen consumption (Table 2). The Gibbs Free Energy of each reaction was also calculated to determine if the reactions were thermodynamically stable as written. Of the reactions considered the oxidation of Fe $S_{(s)}$ (Acid volatile sulfide), NH_4^+ (ammonium), and CH_4 (methane) have the greatest potential of increasing oxygen consumption.

Table 2. Possible Chemical Reactions

No.	Reaction	ΔH^+ As Written	ΔH^+ Assuming Fe^{2+} OR $Fe^{3+}Fe(OH)_3$	ΔG_r° As Written	ΔG_r° Assuming Fe^{2+} OR $Fe^{3+}Fe(OH)$
1	$FeS_{(s)}$ $Fe^{2+} + SO_4^=$	0	+4	-174.32	-356.59
2	$FeS_{(s)}$ $Fe^{3+} + HS^-$	-4	-2	-9.27	4.11
3	$S_{(s)}$ $SO_4^=$	+4		-241.30	
4	$S_{(s)}$ HS^-	-2		119.40	
5	$FeS_{2(s)}$ $Fe^{2+} + SO_4^=$	+2	+8	-269.29	-572.53
6	$FeS_{2(s)}$ $Fe^{3+} + S^=$	-2	-8	211.79	223.84
7	$FeS_{(s)}$ $Fe^{3+} + SO_4^=$	-2	+4	-369.97	-640.04
8	$FeS_{2(s)}$ $Fe^{3+} + SO_4^=$	+2	+8	-642.40	-644.53
9	NH_4^+ NO_3^-	+2		-64.12	
10	Fe^{2+} Fe^{3+}	-4	+8	-42.26	-15.90
11	CH_4 $H_2()_3$	+1		-193.55	
12	Fe^{3+} $Fe(OH)_3$	-3		6.95	
13	Fe^{2+} $Fe(OH)_3$	+4		-7.95	

METHODS

Equipment

All but one of the tests performed were conducted in microcosms used by McCall and Fisher (1980) and subsequently modified for the present research (figure 1). The modification consisted of making two-piece cylinders which were connected by a threaded, polycarbonate coupling. The purpose of the modification was to facilitate the slicing of sediment core sections for pore water analyses.

The other test was conducted in a respirometer made from a polycarbonate tube of about 12.65 cm in length with an inside diameter of 2.54 cm and a wall thickness of 0.16 cm. One end of the tube was permantly sealed with a polycarbonate dish. The other end was threaded and fitted with a polycarbonate screw cap through which a hole was drilled for insertion of the oxygen electrode.

All oxygen measurements were made with a transidyne General Corporation Type 731 Clark-Style electrode connected to a Transidyne General Corporation Chemical Microsensor. Data were recorded on an Esterline Angus strip-chart recorder.

Before initial use of the elctrode a two point calibration was performed. The electrode was inserted into a beaker of water into which air was bubbled. When the electrode reaching stabilized, a gain adjustment was made to make the reading 21%. The electrode was then inserted into a beaker into which N_2 was bubbled and in which sodium sulfite had been added (to combine with dissolved oxygen). When the electrode reading stabilized ($\simeq$ 1%), a zero adjustment was made to make the reading 0%. Then before each test, the 21% point (saturation) was checked, and the gain was adjusted as necessary.

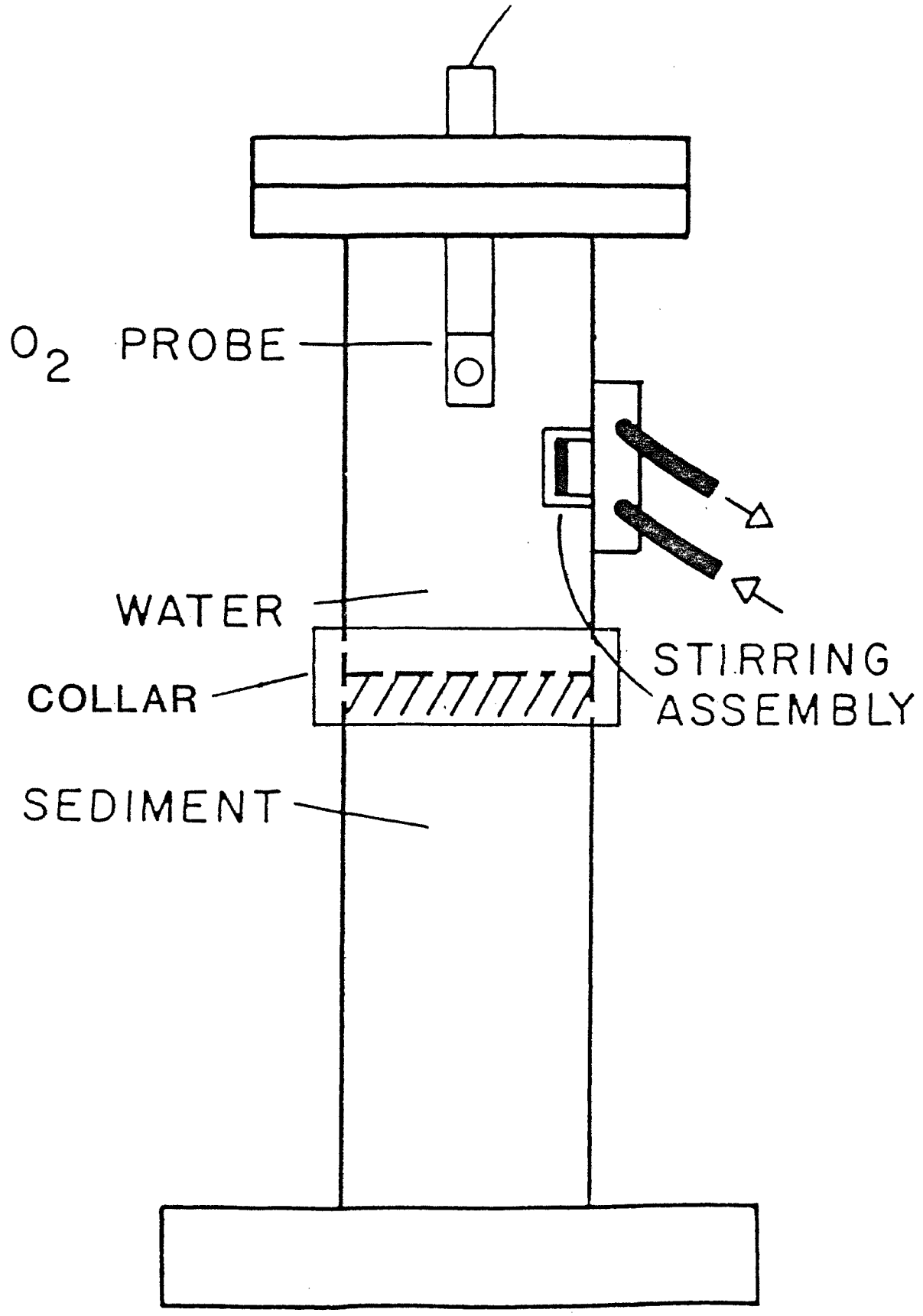


Figure 1.: Typical configuration of microcosm used for experimental oxygen consumption measurements.

Experimental Animals

Tubificid oligochaetes were used for all of the experiments involving macrobenthos. Most of the Oligochaetes came from the mouth of the Cuyahoga River; however some did come from the Western basin of Lake Erie. No attempt was made to use a particular species.

Experimental Sediment

Two sediments were used in the experiments: one was natural Lake Erie sediment from the Western basin of Lake Erie which was sieved before use; the other was Kaolin, which was purchased commercially. Median particle diameter and organic carbon content were not determined for these sediments.

Procedure

In order to estimate values for the components of sediment oxygen demand a number of tests had to be performed. It was necessary to measure the respiration of oligochaetes, the oxygen consumption of sieved Lake Erie sediment with and without oligochaetes present, the oxygen consumption of irradiated (about 5 megarads of gamma radiation from a cobalt 60 source) sieved lake sediment and the oxygen consumption of oligochaete fecal pellets. All of the tests except for the fecal pellet test have been conducted.

Oligochaete respiration was measured by two methods: One measured oxygen consumption in a respirometer with no substrate, and the other in a microcosm with kaolin as a substrate. A sample of water from both the respirometer and the microcosm was analysed for NH_4^+ after each test.

To measure the combined chemical and bacterial oxygen demand of lake sediment at steady-state, sieved Lake Erie sediment was used in a series of tests. The oxygen consumption of a sample of sieved sediment was measured at intervals over a period of 2-3 weeks. Sieved Lake Erie sediment was placed in a microcosm, generally filled with "aged" tap water

(tap water stored in an uncovered container for a minimum of 10-12 hours) and allowed to settle. Time was measured from the filling of the microcosm with sediment. Initially sediment oxygen demand was high, but it declined to a relatively constant value over a 2-3 week period. This change in oxygen demand is assumed to be caused by two factors: 1) After the sediment is sieved or homogenized, there is a significant increase in the population of bacteria, which declines to a relatively stable level over a period of 2-3 weeks, and 2) the process of homogenizing brings reduced species to the surface where they are ozidized. The oxygen consumption data were plotted; then data from earlier tests were plotted on the same axes; and an envelope curve, shown in figure 2 was constructed using all of the data. All of the data were corrected to 20^{0}C.

Oligochaetes (130) were then added to the microcosm containing sieved sediment to simulate a material lake core. Air was bubbled in to keep the overlying water saturated with oxygen. After the oligochaetes had burrowed into the sediment, the air bubbler was removed and the microcosm was sealed and several tests were performed to measure the oxygen consumption of simulated natural lake sediment.

In an attempt to estimate the contributions of microbial respiration and chemical oxygen demand to total SOD, the microcosm containing the oligochaetes in sieved sediment and a second microcosm containing sieved sediment only were subjected to gamma radiation. These irradiation was performed at the Phoenix Reactor Lab of the University of Michigan under the supervision of Mr. Jack Jones. Both microcosms were irradiated at the same time by a cobalt 60 gamma radiation source for 113 hours. The radiation dose varied over the length of the microcosm but was approximately

5 megarads. During irradiation some of the water in each micorcosm dissociated and the gases escaped through a vent in the cover of each microcosm that was cracked open for that purpose. Water was added to each microosm to make up what had been lost. The two microcosms were tested serially, and the data were added to the curve, figure 2.

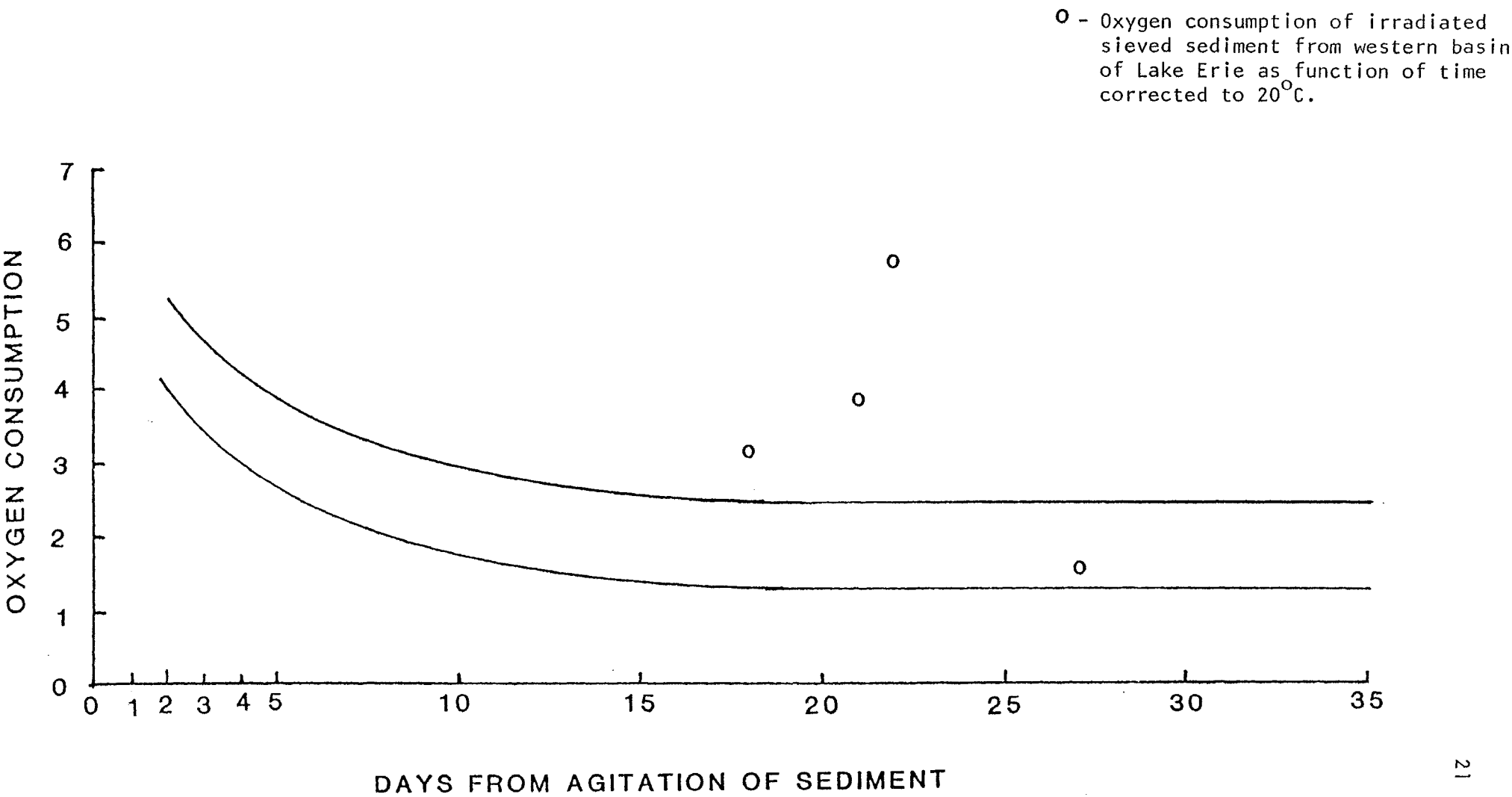
Partly because non-sterile water was used in the previous two tests, the sediment in the microcosms was stirred to mix it up, some sieved sediment was added, the microcosms were filled with "aged" tap water and sealed, and both micorcosms were again irradiated. This time the period of irradiation was about 166 hours and the dose was greater than 5 megarads. During these two tests the radiation damaged the microcosms, which began to leak. Each microcosm was wrapped with several layers of plastic tape to control leaking, sterilized water was used to fill the microcosms, and tests to measure SOD for each microcosm were conducted serially. Although the leaks were reduced a good deal, they were never completely stopped. Therefore relatively short tests were performed serially to measure SOD. Because the tests were short, it is assumed that the data from these tests is reasonably good. These data were also plotted on Figure 2.

Subsequently a core of sediment was removed from the microcosm that contained no oligochaetes and an analysis was performed to measure the concentration of NH_4^+ out of the sediment.

Only part of the sediment from the core was used to analyze for NH_4^+. The balance of the sediment was labeled and stored in a freezer for a future analysis for acid voltatile sulfide, (FeS) which is a reduced solid

FIGURE 2

Microbial and chemical oxygen consumption of sieved sediment from western basin of Lake Erie as function of time corrected to 20° C.



species that will consume oxygen when it is transported to the sediment surface in oligochaete fecal pellets.

As was noted in the Introduction one of the reasons for doing this research is to enable environmental managers to construct more realistic models of oxygen depletion in lakes. Therefore, oxygen concentration profiles were calculated from the models and compared to the profiles measured by Revsbech et al. (1980) for one case.

RESULTS

Oligochaete Respiration

In preliminary reports a value of oligochaete respiration of 0.061 $\frac{\mu MO_2}{Mg/wet\ mass/day}$ was reported. This value was based on a test which measured the respiration of 35 tubificid oligochaetes in a respirometer described in section on methods. The value is probably somewhat in error for several reasons: 1) the weight of the oligochaetes was determined by an inaccurate method and was probably overstated; 2) drift of the oxygen electrode was not considered; and 3) the concentration of dissolved oxygen, 9 mg/ℓ, was an assumption, because temperature and pressure were not recorded. The concentration assumption is probably reasonable because the respirometer was suspended in water that was controlled at 20°C. Even if the water temperature varied between 19-21°C and the barometer between 28.5 - 30.5 inches of mercury, the dissolved oxygen concentration would only vary by about ± 5%. Using an estimated weight of the 35 oligochaetes of 96.2 mg based on the weighings of 60 oligochaetes in 6 groups of 10 each and an estimated drift rate of 0.06% per hour a new value of oligochaete respiration of 0.079 $\frac{\mu MO_2}{Mg\ wt\ mass/day}$ was calculated. A sample of water was withdrawn from the respirometer and analysed for ammonium ion, NH_4^+. A concentration of about 38 µmol/l was found. As it is unlikely that significant concentrations of NH_4^+ would exist in water saturated with oxygen, this finding suggests that the oligochaetes secreted the NH_4^+ directly.

Several other tests were conducted to measure oligochaete respiration in a microcosm containing kaolin as a substrate. On one of these tests when everything seemed to work reasonably well, oligochaete respiration was found to be 0.061 $\frac{\mu MO_2}{Mg\ wt\ mass/day}$. On another test for which oligochaete respiration was not calculated, a concebtration of about 10-15 µ Mol/ℓ of

NH_4^+ was found. This concentrationvalue of NH_4^+ in a microcosm containing Kaolin may well be low because NH_4^+ would probably adsorb to Kaolin.

These values of oligochaete respiration are larger than the value found by McCall and Fisher (1980). Their value was 0.01 $\frac{\mu MO_2}{\text{Mg wet mass/day}}$.

Chemical and Microbial Oxygen Demand

A series of 5 tests were conducted with sieved sediment from the western basin of Lake Erie to establish a steady-state value or range of values for oxygen consumption due to chemical and microbial demand. Sieving the sediment eliminates oligochaetes. These data were plotted as a function of time and then other data generated withoug this purpose in mind were also plotted, and two curves (Fig. 2) were then drawn to envelope the data. From these curves the oxygen consumpion at steady state (14-21 days) ranges from about 1.25-2.50 $\frac{\mu M\ O_2}{Hr}$. McCall and Fisher (1980) showed a value of 2.26 $\pm$ 0.03 $\frac{\mu\ Mol\ O_2}{Hr.}$. The upper range of oxygen consumption reported here agrees very well with Fisher.

Chemical and Microbial Oxygen Demand + Oligochaete Respiration

Two tests were also performed with 130 oligochaetes added to the microcosm containing sieved sediment. These tests simulate a natural lake core with a population of about 28,500 tubificid oligochaetes per square meter. Oxygen consumption for one of the tests was 1.53 $\frac{\mu Mol\ O_2}{Hr}$, and the other was 3.46 $\frac{\mu\ Mol\ O_2}{Hr}$.

There is one assumption here that should be made explicit: steady-state for the sediment was reached before the tests with the oligochaetes were performed. The assumption is reasonably good considering that two sediment-only tests totalling 40 hours were performed before the oligochaetes were added and also considering a number of time lags for such things as calibrating the electrode before each test, allowing time for the sediment to settle initially, selecting the oligochaetes for the tests, and

allowing time for the oligochaetes to burrow into the sediment.

It is not possible to compare these total oxygen consumption values with McCall and Fisher (1980), because they used 456 oligochaetes, but it is possible to scale-up the values reported here and compare them with their value. The average weight of the oligochaetes used in this test was 0.00205 g, based on 3 weighings of 10 oligochaetes each from the population of oligochaetes from which the test specimens were taken. The weight of the 130 oligochaetes is 266.5 Mg (130 x 2.05 Mg) and the oxygen consumed by them is $0.7782 \frac{\mu Mol\ O_2}{Hr} \left(\frac{0.061+0.079}{2} \times \frac{266.5}{24}\right)$. Now adding the upper range of chemical and microbial consumption ($2.50 \frac{\mu Mol\ O_2}{Hr}$ and oligochaete respiration together gives an estimate value for a natural lake core of $3.28 \frac{\mu Mol\ O_2}{Hr}$ subtracting this value from 3.47 leaves $0.19 \frac{\mu Mol\ O_2}{Hr}$ that could be assumed to be related to reduced material transport to the surface. If it is also assumed that both oligochaete respiration and the oxidation of reduced material transported to the surface are proportional to the number of oligochaetes present and that the oligochaetes used by McCall and Fisher (1980) are similar in size to the ones used here (McCall and Fisher (1980) noted that the oligochaetes were from Cleveland Harbor) then these values can be scaled-up to 456 oligochaetes. An estimate of the oxygen consumption of the simulated natural lake core would be $5.90 \frac{\mu Mol\ O_2}{Hr} \left[\frac{456}{130} (0.78 + 0.19) + 2.50\right]$ McCall and Fisher (1980) reported a value of $6.72 \pm 9,93 \frac{\mu Mol\ O_2}{Hr.}$, and the derived value shown here compares reasonably well with McCall's and Fisher's value.

Chemical Oxygen Demand

In an attempt to separate chemical from microbial oxygen demand or consumption, two microcosm's one containing sieved sediment only and the other containing sieved sediment plus 130 oligochaetes were irradiated

todestroy bacteria and benthos. The irradiation was performed under the supervision of Jack Jones, at the University of Michigan's Phoenix Laboratory reactor. The source was cobalt 60 which is a gamma ray emitter. Both microcosms were irradiated for 113 hours and received a dose of approximately 5 megarads which is enough to destroy both benthos and bacteria. During irradiation some of the water in each micorcosm was lost as vapor through a part in the cover of each microcosm. The port is sealed during tests to measure oxygen consumption, but was cracked open during irradiation to avoid a pressure buildup in the microcosm.

As was noted earlier, unsterile water was added to each microcosm before performing tests to measure oxygen consumption. The tests were performed serially. The first microcosm to be tested was the one without oligochaetes, and the test was performed within several days after irradiation. The microcosm with oligochaetes (presumably destroyed by the radiation) was tested about 5 days after the first. The oxygen consumption of the sediment in the first microcosm was found to be 3.93 $\frac{\mu Mol\ O_2}{Hr}$ and that of the sediment in the second micorcosm was 1.62 $\frac{\mu Mol\ O_2}{Hr.}$. There is considerable variation in the data, and one of the data points fits the steady-state curve reasonably well, the other data point does not. It may be that the introduction of unsterile water coupled with the time elapsed between irradiation and test allowed bacteria to repopulate the microcosms. Prior to the start of each test, the water in each microcosm was saturated with oxygen by bubbling air into the water; however a filter was placed in the air line to avoid introducing bacteria with the air.

Because of the possibility of having contaminated the microcosms with bacteria, the microcosms were returned to the University of Michigan to be irradiated a second time. Before the microcosms were returned, the sediment was stirred up and some additional sieved sediment was added to compensate for settling that had occurred. Sediment depth controls the depth of the water column which is circulated by a magnetic stirrer, mounted on an inside wall of the microcosm, to avoid oxygen concentration gradients.

The irradiation procedure was the same as the first procedure except that the mirocosms were irradiated for 166 hours and the dose was in excess of 5 megarads. The two microcosms were run serially to measure oxygen consumption. The oxygen consumption of the sediment in the microcosm that had originally contained oligochaetes was meaured first and was found to be $3.2 \frac{\mu Mol\ O_2}{Hr}$. The oxygen consumption of the sediment in the microcosm without oligochaetes was measured about 5 days later and was found to be $5.72 \frac{\mu Mol\ O_2}{Hr}$. These data also show considerable variation, and again one data point fits the steady-state curve reasonably well while the other does not.

As stated earlier, the purpose of irradiating sediment samples was to separate chemical from microbial oxygen demand or consumption. It seems reasonable to assume that chemical oxygen consumption would fall below the lower steady-state curve for combined chemical and microbial oxygen consumption and would be relatively constant over the period of time covered by these tests. The oxygen consumption values of the 4 samples of irradiated sieved sediment are not consistent with these assumptions. It is interesting to note that the samples of sieved sediment that originally contained oligochaetes consumed less oxygen than did the sediment without oligochaetes; however the significance of

this observation is not apparent.

There was no reduction in bacteria counted by epiflourescent microscopy in the water from the first two microcosms from what would be a representative population. However, there was a reduction in the microorganisms from the second two microcosms of about a factor of 10. These findings suggest that there should have been less oxygen consumed in the second set of microcosms.

As part of the attempt to understand the irradiated sediment data, a core was taken from the microcosm without oligochaetes to analyze for the concentration of ammonium ion, NH_4^+, in the pore water to calculate the percent of total oxygen consumption used to oxidize NH_4^+. This analysis was performed about 2 months after the oxygen consumption of the second set of irradiated sediment samples was measured. We used the method of Solarzano (1969). Twelve 1 cm sections were taken from the core. The pore water was extracted using a centrifuge and diluted to 5 ml. A sample of the overlying water was also taken. To each water sample were added ethanolic phenol, sodium nitroprusside and a mixture of alkaline sodium citrate and sodium hypochlorite (chlorox) were added in that order with mixing in between. After a minimum of one hour but within about 3-4 hours, the absorbance of blue indophenol that formed was measured using a spectrophotometer at 640 nm. Concentrations were determined from a standard curve of concentration vs absorbance prepared for that purpose. Fick's first Law of Diffusion was then used to calculate the flux of ammonium out of the sediment, and the flux was used to calculate the amount of oxygen used to oxidize all of the ammonium. The calculated flux, F_i, is $608.24 \frac{\mu Mol\ NH_4^+}{M^2\ day}$. Two moles of oxygen are needed to oxidize each mole of NH_4^+; therefore 1216.48 moles

of oxygen are consumed. This amount of oxygen represents 9.25-18.5% of the range of oxygen consumed by sieved sediment at steady-state as found by this experimental work. This range compares reasonably well with the 15% found for sediment from the western basin of Lake Erie (Personal observation of Dr. Matisoff).

A portion of each core section taken for the ammonium analysis was frozen and will be used later for an analysis of acid volatile sulfide, FeS.

Oxygen Consumption Models

In an effort to construct models to predict oxygen consumption, we modelled the oxygen profiles for one of the cases described in the paper by Revsbech, et al., (1980).

Steady-state profiles (Bouldin, 1968; Murray and Grundmanis, 1980) as well as transient profiles (Bouldin, 1968; Revsbech et al., 1980) have been used to calculate the flux of oxygen across the sediment-water interface. These previous models all require assumptions about the kinetics of the reactions that consume oxygen in sediments. We present here different models here different models of the time dependent data presented in the excellent paper by Revsbech et al. (1980) to determine the kinetics and rates of oxygen consumption in sediments. In addition, these models will permit a comparison of the results obtained from steady-state and transient data and a comparison of the calculated sediment-oxygen-demand (SOD) based on different kinetic formulations.

For the purpose of this exercise, the 10^{0}C dark data was selected from Revsbech et al. (1980) (their Fig. 3A). This data has been redrawn and is presented in Fig. 3. This experiment consisted of illuminating the sediment surface and periodically recording the oxygen profiles

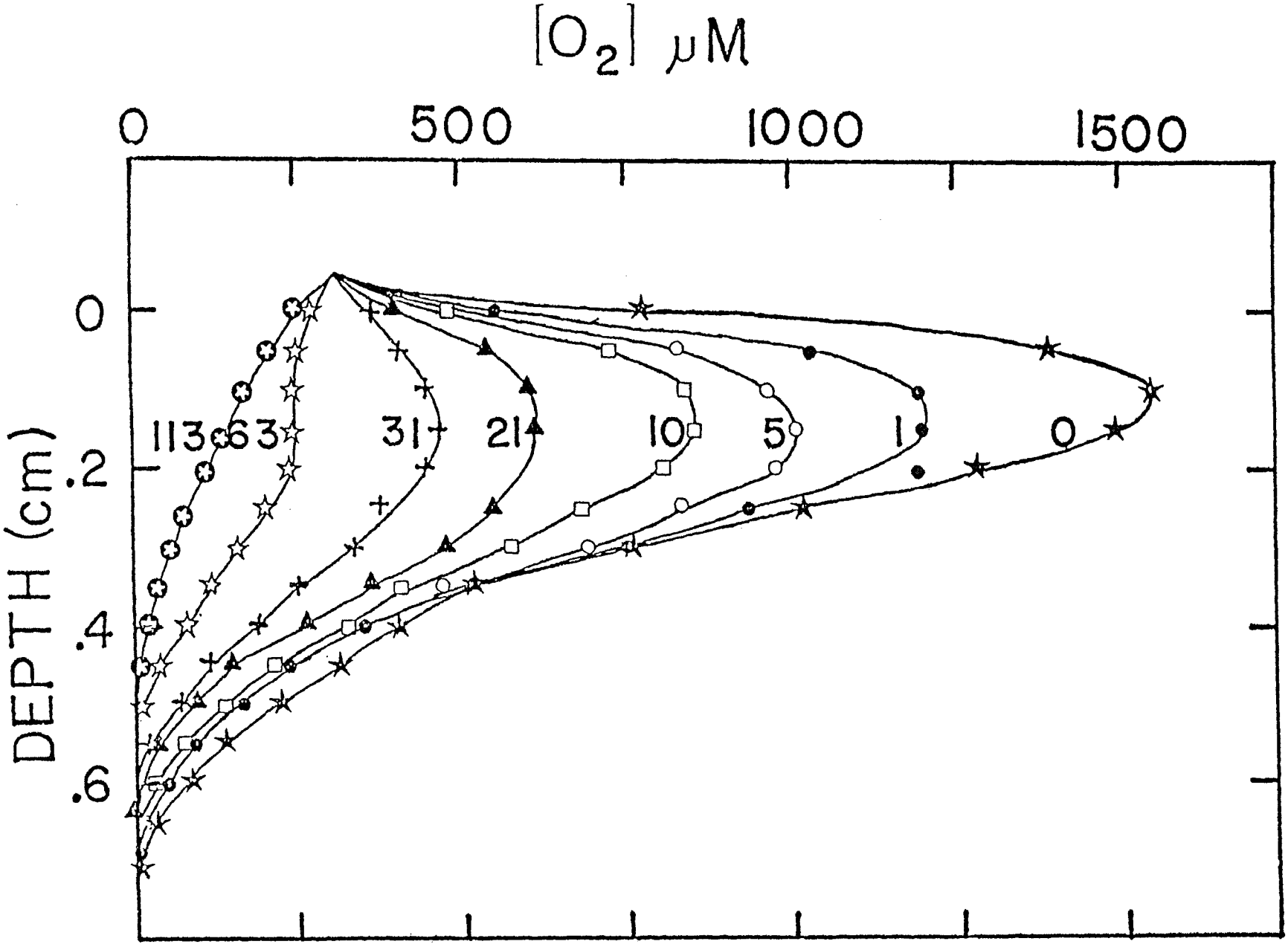


Figure 3

Time series of oxgen profiles in recent marine sediments reported by Revsbech et al., (1980). Subsurface maximum at t = 0 caused by benthic photosynthesis prior to extinguishing the light. Steady-state observed at 113 minutes.

after the light had been extinguished (time t = 0). The oxygen profiles have a subsurface supersaturation caused by benthic photosynthesis. In the dark, the transient profiles of oxygen concentration show a decrease over two hours to steady state.

Mechanisms for oxygen removal in sediments include diffusion and consumption by reaction. Oxygen in pore waters may be removed by microbial and macrobial respiration; reaction with a counterdiffusing reductant (Bouldin, 1968); reaction with reduced solids (McCall and Fisher, 1980); and in the case of supersaturation, the upward movement of gas bubbles. Adams, Matisoff, and Snodgrass (in press) suggest that about half of the sediment-oxygen demand in Lake Erie could be accounted for by the oxidation of counter diffusing ammonium and methane. The mechanisms of metabolic reactions are extremely complex and most likely the consumption of oxygen is the result of many biologic and abiologic reactions. For the purposes of modeling oxygen profiles and calculating sediment-oxygen demand, the majority of the oxygen consumption can be assumed to be caused by microbial respiration (Murray and Grundmanis, 1980).

The concentration of dissolved oxygen in the interstitial water of sediments may be described by the diffusive flux of oxygen (into the sediment when $C_{sed} < C_{surface}$) and consumption caused by respiration:

$$\frac{\partial C(z,t)}{\partial t} = D' \frac{\partial^2 C(z,t)}{\partial z^2} - \left.\frac{\partial C(z,t)}{\partial t}\right|_b \qquad (1)$$

where C(z,t) is the concentration of dissolved oxygen as a function of depth and time, t is time after extinguishing the light, z is depth in the sediment (positive downward), D' is the apparent diffusion coefficient of oxygen in the sediment (constant porosity assumed) and $\left.\frac{\partial C(z,t)}{\partial t}\right|_b$ is the rate of consumption of oxygen by respiration.

In this work, three common kinetic descriptions for removal by respiration are considered. Zobell and Stadler (1940) report no influence of oxygen tension on respiration rates of lake bacteria, i.e., the consumption reaction is zeroth order:

$$\frac{\partial C(z,t)}{\partial t} = R \tag{2a}$$

where R is a constant rate of consumption of oxygen. Many reactions are more accurately described by first order kinetics, where the rate of the reaction is proportional to the amount of reactant:

$$\frac{\partial C(z,t)}{\partial t} = RC(z,t) \tag{2b}$$

When the uptake of a solute is mediated by an enzymatic reaction located on or in the cell membrane, the rate of uptake can be described by Michaelis-Menten kinetics:

$$\left.\frac{\partial C(z,t)}{\partial t}\right|_b = \frac{R_m C}{K_m + C} \tag{2c}$$

Where R_m is the miximum rate of reaction, attained when uptake sites are continually saturated with substrate; K_m is the Michaelis constant, by definition the substrate concentration when the rate of reaction is exactly one-half the maximum rate R_m.

The solution to equations (1) and (2) requires initial and boundary conditions. The initial condition is simply the time t=0 profile measured immediately after the light was turned off. That concentration profile is represented by a line segment from the overlying water to the sediment-water interface, and as a gaussian below. This describes the data around the subsurface maximum very well. The upper boundary condition is that the concentration in the overling water is constant

and equal to the saturation concentration (299 μ Moles O_2/ℓ at 10^oC). The lwoer boundary condition is that there is no flux of oxygen at infinite depth (represented numerically as 1.4 cm).

Equations (1) and (2) were solved numerically using the above initial and boundary conditions by an explicit finite-difference approximation. In order to insure accuracy and stability, Δz was set equal to 0.01 cm and Δt set equal to 5 sec. The value of D' used was 9.0×10^{-6} cm^2/sec, in agreement with previously used values of D' of oxygen in sediments and soils ($D'=1 \times 10^{-5}$ cm^2/sec, Bouldin, 1968; $D'9.0 \times 10^{-6}$ cm^2/sec, Revsbech et al., 1980; $D' = 6.0 \times 10^{-6}$ cm^2/sec, Murray and Grundmanis, 1980). The calculated profiles were similar for all three cases; the results for first order kinetics are presented in Fig. 4.

Since none of the models could reproduce the data (Fig. 3) exactly, the coefficients were varied in the rate equations to match either the observed 1 min profile (O_2 max ~1200 μM) or steady-state (113 Min) profile (O_2 ~0 at z=.5 cm). In all three cases the rates of removal required to match the 1 minute profile are substantially larger than those needed at longer times. Conversely, if the steady-state profile is matched, then the calculated transient fprofiles show less consumption of oxygen than the data.

There are several possible explanations for the discrepancy between the observed and calculated profiles. First, the measured data for the short time intervals could be in error since the time of measuring a complete profile is long with respect to the reported time. This is possible for the 1 minute profile, but since the error decreases with increasing time it should be small for profiles >5-10 min. In addition, Revsbech, et al. (1981) present transient profiles that are similar to those in Fig. 3 and were recorded within about 10 sec. Thus, although there may

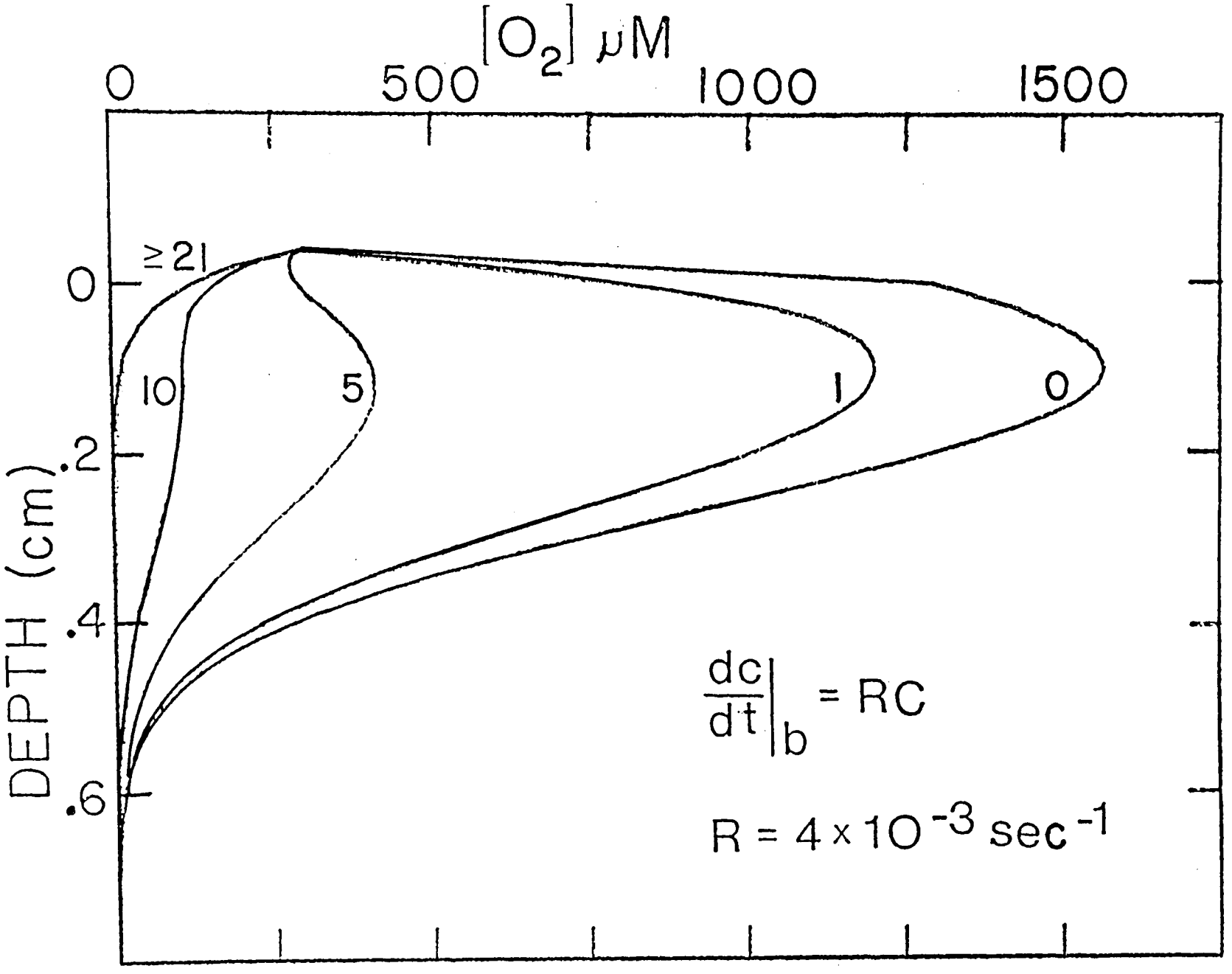


Figure 4A

Oxygen profiles simulated by equations (1) and (2b). First order removal rate constant = 4 x 10^{-3} sec^{-1} selected to match the 1 min oxygen concentration maximum ≈1200 µM.

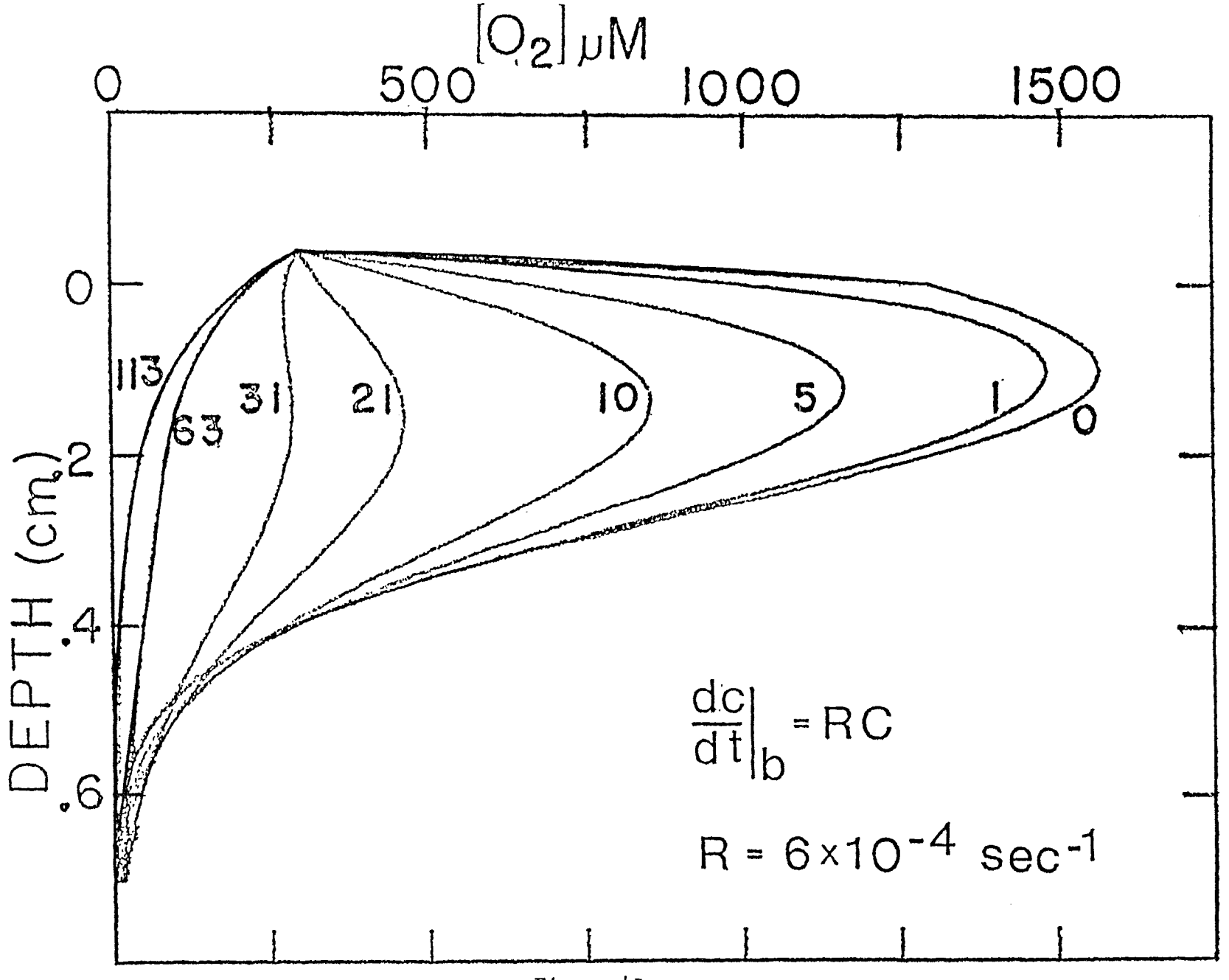


Figure 4B

Oxygen profiles simulated by equations (1) and (2b). First order removal rate constant = 6×10^{-4} sec^{-1} selected to match oxygen concentration, ~0 µM at .5 cm at 113 min.

be some error in the early data it seems unlikely that measurement error alone can account for the discrepency. A second possible explanation is that the rate expressions in equation (2) are incorrect. These are the most commonly used kinetic expressions and have been used successfully to describe many chemical and microbial reactions (Berner, 1980). This suggests that the data should be reasonably accurately described by one or more of these kinetic expressions. A third possibility is that physical or chemical processes not included in equation (1) are important. These processes could include the effects of stirring (Revsbech et al., 1980), advection of pore water or sediments by organisms (Murray and Grundmanis, 1980) chemical reaction with reduced compounds, bubble ebullition, and variable organic matter and porosity values with depth. The calculated transient profiles based upon a match with the steady-state profile suggests that an increased rate of exchange in the upper portion of the sediment column could account for the discrepancy. Revsbech et al., (1980) indicated that they tried to examine samples that were not actively affected by organisms even though the sediments were bioturbated. This suggests that advection of pore water or sediments and variable organic matter are unlikely causes of the discrepancy. The effects of stirring and variable porosity could cause increased exchange with the overlying water without an increased consumption rate, but it seems unlikely that these processes could account for the factor of 5-10 needed. Consumption of oxygen by reaction with reduced compounds (both solid and dissolved) and bubble ebullition could account for the increased exchange. This means that the values selected to match the steady-state profile are closer to the true values than the transient profiles would indicate. Because of the lack of additional information, such as the porosity variation with the top 7 mm or the quantity of reduced species oxidized, it was not possible to include these effects in the model.

The sediment-oxygen-demand has been calculated for each of the three kinetic expressions and is given in Table 3. The calculated SOD for each of the kinetic expressions matched to the same profile agrees to within a factor of 3-4. As indicated above, the rates determined from matching the steady-state profile are probably more accurate, and consequently, the SOD values calculated from them are probably more accurate. These values range from 0.5-1.5 mMoles/m^2 hr. Revsbech et al., (1980) utilized a portion of the observed transient data, assumed zeroth order kinetics, and reported a value of 17.5 mMoles/m^2day (=0.7 mMoles/m^2 hr), in excellent agreement with the value reported here. This is much higher than the 9.0 x 10^{-14} Moles/cm^2 sec (=3.2 x 10^{-3} mMoles/m^2hr) reported for pelagic sediments by Murray and Grundmanis (1980), which probably reflects a relationship between easily metabolizable organic matter and SOD.

In conclusion, transient proewater-profiles of oxygen provide a sensitive constraint for the processes affecting oxygen in sediments. The modeling of transient experimental data indicates an oxygen removal mechanism other than diffusion and biological respiration. Although steady-state profiles do not provide a sensitive means to determine the kinetics of the oxygen consumption reactions, they do permit an accurate determination of the sediment-oxygen-demand regardless of the assumed consumption.

Table 3

Comparison of sediment-oxygen-demand calculated for each of the three kinetic expressions from rates determined from matching the 1 minute and steady-state (113) min profiles.

$\frac{\partial c(z,t)}{\partial t}\Big\|_b$	SOD (1 min) $\left(\frac{\text{m Moles}}{m^2\ hr}\right)$	SOD (steady-state) $\left(\frac{\text{m Moles}}{m^2\ hr}\right)$
R	59.2	0.5
RC	14.1	1.5
$\frac{R_m C}{K_m + C}$	22.1	1.4

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